Changes in Trace and Minor Constituents and Associated Micro-architecture of *Montastrea faveolata* during Time of "Stress"

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Abstract:

As corals grow, they secrete a calcareous skeleton with the aid of photosynthetic activity of endosymbiotic dinoflagellates. The rate of this secretion varies annually which produces annual bands. Entrapped with the carbonate are trace substances that record the chemistry of the surrounding ocean. Detailing these changes in chemistry requires careful high-resolution sampling. New procedures involving laser ablation inductive couple plasma mass spectroscopy (LA-ICP/MS) provides a unique method that does not involve tedious sample preparation. The La-ICP/MS data for a series of Atlantic corals from Looe Key, U.S. Florida Keys shows an intriguing distribution trace and minor elements whose concentrations are related to reported bleaching events. SEM data from the layers exhibit a change in crystal habit concurrent with the changes in chemistry. These changes reflected the affect of the variable influence of the symbiotic algae on the development of the coral skeleton.

Introduction

Its is generally agreed that the skeleton of scleractinian (stony) corals is constructed of aragonite and that there are recognizable annual bands of high and low density. Although governed by mineralogical rules of crystal growth, the aragonite crystals are considered biocrystals produced by organic processes. Growth is thought to occur along the boundary between the ectoderm and the skeleton with photosynthetic activity of endosymbiotic dinoflagellates (commonly called zooxanthellae) playing a major role. During biomineralization, the carbonate skeleton incorporates elements and partitions isotopes from the surrounding water, thereby recording the environmental conditions under which the coral skeleton was formed.

Many studies have established the advantages of analyzing a suite of tracers from each coral skeleton, allowing the simultaneous determination and decoupling of a range of environmental variables[1-11]. High-spatial resolution analysis of the coral skeleton composition permits the detection of seasonal and shorter timescale events, such as freshwater flood pulses, which often have duration of a few weeks or less. Techniques for high-resolution analysis of coral skeletons are of two major types: 1) high precision drilling of samples with processing and analysis carried out in solution[2,6], or 2) analysis of the coral in the solid state by microbeam methods such as ion microprobes[10-15]. The milling and subsequent analysis of the solution method is time consuming, requiring many steps which can lead to contamination especially when attempting to measure trace metals present in very low concentration. The microbeam methods however are fast and give high resolution. One microbeam technique that is becoming widely used for geological samples is laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS).

Method

During the summer of 2002, 24 short coral cores were obtained along the fore reef at Looe Key, in the Florida Keys (Fig.1). These cores of the genus and species *Montastrea faveolata.* The minor and trace elements concentrations were determined using a Cetac® laser attached to an Elan® ICP/MS. The system sampled at a scan rate of 50 microns per send with a 100 micron spot size. The $\delta^{13}C$ and $\delta^{18}O$ were determined on samples obtained by a computer controlled micro drill. These samples were collected parallel to the banding and were collected at a frequency of approximately 4 per year. In addition, sections of the corals were photographed with a Scanning Electron Microscope (SEM) where there were significant changes in chemistry and isotopic composition.

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Results

It was determined that the concentrations of boron, magnesium and phosphorous could be correlated between the corals and the highest values correlated with high-density bands. The carbon isotopic signature in high-density bands was determined to be more positive than the signature in the light density bands(Fig2). It was further determined that the highest concentration of boron, magnesium, and phosphorous and the heaviest carbon isotopic signature occurred at the time of significant temperature increases.

It is well known that the boron species in seawater is related to pH and it has been demonstrated that at times of high pH, boron is increasingly assimilated into the coral structure. This increase also correlates with an increase in ^{13}C in the skeleton. Previous investigators have suggested that this phenomenon is the result of the physiological processes leading to the precipitation of the carbonate structure driven by the photosynthetic zooxanthellae [16]. In the Looe Key corals, the δ^{13}C ranges from $-2^0/_{00}$ to $-3^0/_{00}$ in the low density portion of the skeleton reflecting an influence of zooxanthellae photosynthesis. However, during the formation of the high-density bands the δ^{13}C approaches 0, suggesting a limited or no photosynthetic effect. In addition, the heavier δ^{13}C is associated with elevated magnesium and phosphorous concentrations. These observations suggest that during the times of stress the high-density bands are deposited in a high pH environment (mostly inorganic aragonite crystals), while the light bands are formed in a photosynthetic driven environment forming biocrystals of aragonite.

SEM images of the regions of high boron, magnesium, phosphorous and high density showed the presence of crystals (approximately 10 microns in diameter) which have a different habit than the normal aragonite forms. These crystals were found to have a high magnesium content and have a microcrystalline habit similar to dolomite or magnesite (Fig3). At the present, due to the small size, the structure of these minerals is unknown, but is presently under investigation and open to speculation.

In the twenty corals analyzed, the combination of high magnesium, boron, and phosphorous, coupled with the heavier carbon isotopes and microcrystalline structure occurs at all the times of reported bleaching events during the last decade. These characteristics are particularly strong during the 1998 El Nińo bleaching event. It thus appears that this unique mineralogy and chemistry is related to stress and may be useful in determine historically similar events in the recent geologic past.

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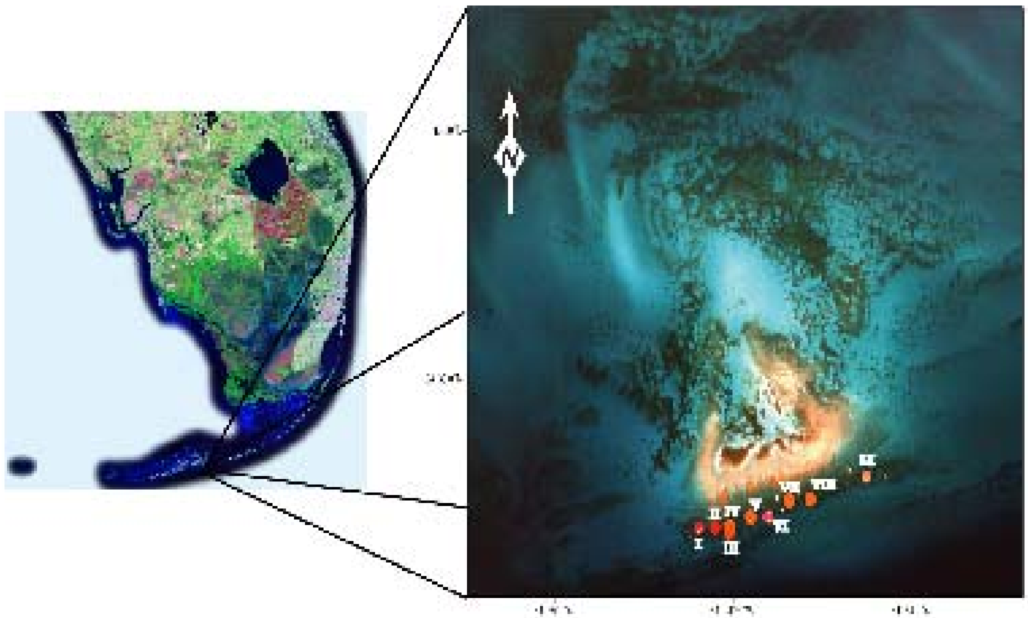

Figure 1 -- Location of cores and Looe Key National marine Sanctuary

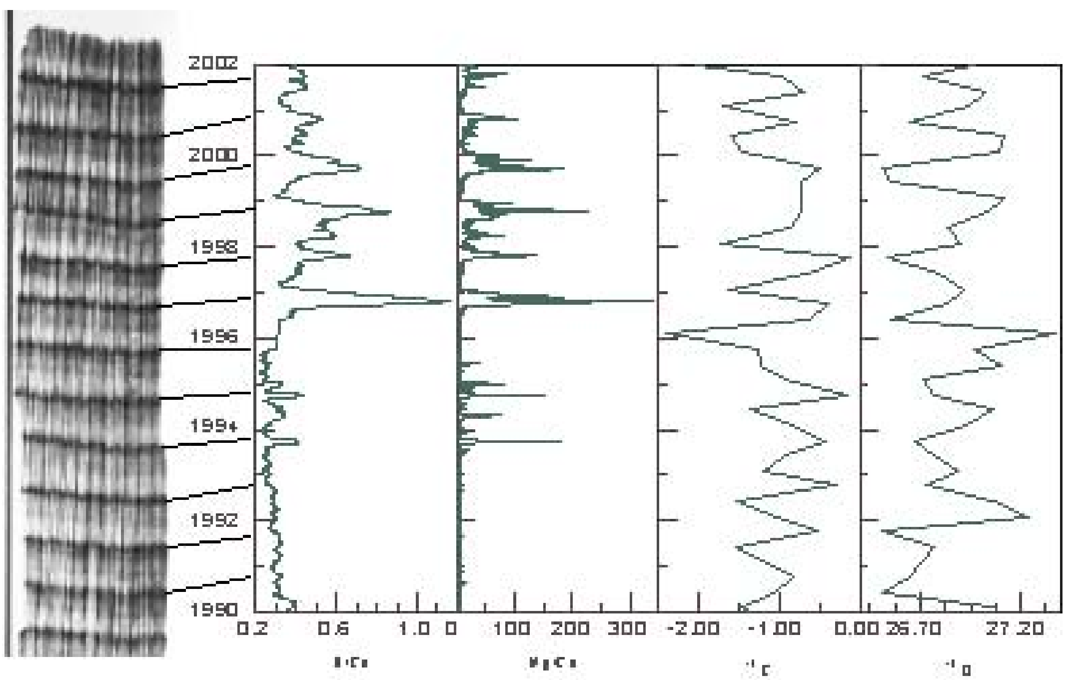

Figure 2 -- The distribution of the boron/calcium and the magnesium/calcium intensity ratios and the $\delta^{13}C$ and $\delta^{18}O$ for the top of coral core 1,(Site IX). This part of the core represent the last twelve years. The high density bands are thought to form during the late summer/early fall and often coincided with the high temperatures.

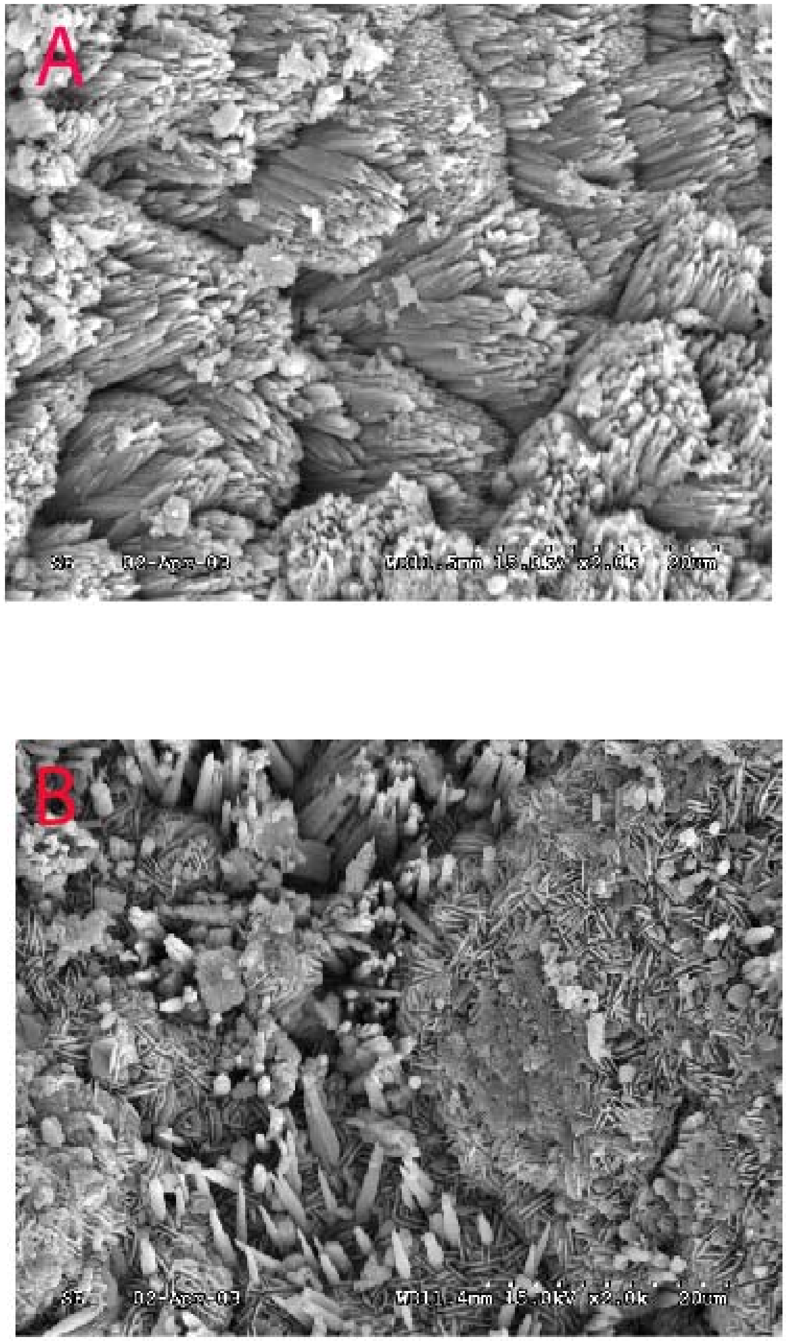

Figure 3 – SEM photo micrographs of acircular aragonite needles found on flank walls of a coral. Exuberant crystals forming bundles represent what is typically seen in a 'normally' growing coral (A). Furher up the coral skeleton, but within the same type of structure, there are numerous unknown crystals between widely dispersed aragonite needles (B). The unknown crystals haave a disnct blade-like habit and have a large magnesium content as determined by energy dispersive spectroscopy.